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Author(s)	
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International Research Center for Elements Science - Organotransition Metal Chemistry -

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Prof
OZAWA, Fumiuyuki
(D Eng)



Assoc Prof
OKAZAKI, Masaaki
(D Sc)



Assist Prof
KATAYAMA, Hiroyuki
(D Eng)



PD
MUTOH, Yuichiro
(D Eng)

Students

NAGAO, Masato (D3)

MURAKAMI, Hiromi (D2)

WAKIOKA, Masayuki (D2)

JENSEN, Rader S (D2)

HAYASHI, Akito (D1)

WATANABE, Emiko (M2)

HAYASHI, Kyohei (M1)

YOSHITOMI, Takahiko (M1)

YOSHIMURA, Ken-ichi (M1)

UEHIRA, Kousei (UG)

YAMAMOTO, Yasutaka (UG)

Scope of Research

This laboratory aims at establishment of new synthetic methodologies and new functional materials by designing well-defined catalysts based on transition metal chemistry. New concepts and ideas of molecular-based catalysts are accumulated by mechanistic investigations using kinetic techniques on the reaction intermediates and elementary processes. The research subjects include: (1) development of novel ligand systems for catalysis, (2) functionalization of organic substrates on transition-metal clusters, and (3) development of highly efficient ways of constructing functional organic molecules.

Research Activities (Year 2005)

Presentations

Stereocontrolled Synthesis of All-cis Poly(phenylene vinylene)s (PPVs): A Novel Method For Direct Micropatterning of PPVs, Ozawa F, The 4th International Symposium of the Kyoto COE Project "Elements Science", 6 - 7 January, Kyoto, Japan.

(Z)-Selective Cross-Dimerization of Arylacetylenes with Silylacetylenes Catalyzed by Vinylideneruthenium Complexes, Katayama H, Ozawa F, The 4th International Symposium of the Kyoto COE Project "Elements Science", 6 - 7 January, Kyoto, Japan.

Stereocontrolled Synthesis and Optical Properties of All-cis Poly(phenylene vinylene)s (PPVs): A Novel Method for Direct Patterning of PPVs, Katayama H, Nagao M, Nishimura T, Matsui Y, Umeda K, Akamatsu K, Tsuruoka T, Nawafune H, Ozawa F, The 8th SPSJ International Polymer Conference (IPC2005), 26 - 29 July, Fukuoka, Japan.

Stereocontrolled Synthesis and Optical Properties of All-cis Poly(phenylene vinylene)s (PPVs): An Extremely Simple Method for Direct Patterning of PPVs, Katayama H, Ozawa F, The 4th Asian-European Symposium, 6 - 9 November, Nagasaki, Japan.

Highly (Z)-Selective Hydrosilylation of Terminal

Alkynes Catalyzed by Diphosphinidene-cyclobutene Ruthenium Complex: Application to the Synthesis of (Z,Z)-Bis(2-bromoethenyl)arenes, Katayama H, Ozawa F, The 13th Korea-Japan Joint Symposium on Organometallic and Coordination Chemistry, 23 - 26 November, Jeju, Korea.

Stepwise Halogenation of Acetylene on the Tetrairon Core: Systematic Synthesis and Property of Haloacetylene-Coordinated Clusters, Okazaki M, Takano M, Yoshimura K, Tobita H, Ozawa F, Singapore International Chemical Conference 4 (SICC-4), 8 - 10 December, The Shangri-La, Singapore.

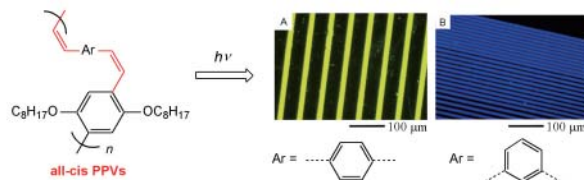
An Ethynyl Cation on the Butterfly-type Tetrairon Core, Okazaki M, Takano M, Yoshimura K, Tobita H, Ozawa F, PACIFICHEM2005, 15 - 20 December, Honolulu, Hawaii, USA.

Alkyne-insertion into *cis*-Pt(ER₃)(SnMe₃)L₂ Complexes (E = Si, Ge), Ozawa F, PACIFICHEM2005, 15 - 20 December, Honolulu, Hawaii, USA.

Highly Active Catalysts Bearing Diphosphinidene-cyclobutene Ligands, Ozawa F, The 6th Journal of Organometallic Chemistry Symposium, 17 - 18 December, Honolulu, Hawaii, USA.

Stereocontrolled Synthesis and Optical Properties of All-cis Poly(phenylene vinylenes) (PPVs): A Method for Direct Patterning of PPVs

Poly(phenylene vinylenes) (PPVs) belong to the group of π -conjugated polymers that have applications in light-emitting diodes (LEDs), lasers, and solar cells. Although stereoregularity of vinylene linkages in the polymer backbone is also known to profoundly affect the optical properties of PPVs, efficient ways of regulating the geometries of vinylene linkages have remained almost unexplored. Geometrically pure, all-cis poly(phenylene vinylenes) (PPVs) are synthesized by Suzuki-Miyaura-type polycondensation of 2,5-dioctyloxy-1,4-benzenediboronic acid with (*Z,Z*)-bis(2-bromoethenyl)benzenes, which are prepared by ruthenium-catalyzed (*Z*)-selective double hydrosilylation of diethynylbenzenes, followed by bromodesilylation of the resulting (*Z,Z*)-bis(2-silylethenyl)benzenes with *N*-bromosuccinimide. The all-cis PPVs thus obtained undergo one-way photoisomerization to the corresponding *trans*-PPVs both in solution and in the solid. This phenomenon is applied to direct microscale patterning of PPVs onto a quartz substrate.

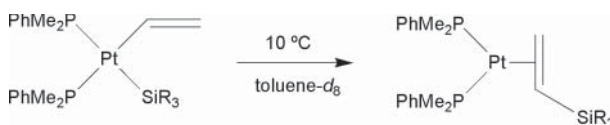


Scheme 1. Fluorescent images of micropatterned all-cis PPVs.

C-Si Reductive Elimination from *cis*-Vinyl(silyl)platinum(II) Complexes

While the transition-metal-catalyzed silylation reactions of unsaturated hydrocarbons such as hydrosilylation, bis-silylation, and borylsilylation are generally assumed to involve C-Si reductive elimination as the product-forming step, detailed information on this elementary process has been limited. The complexes *cis*-Pt(CH=CH₂)(SiR₃)(PMe₂Ph)₂ (R₃=Ph₃, (C₆H₄Me-*p*)₃,

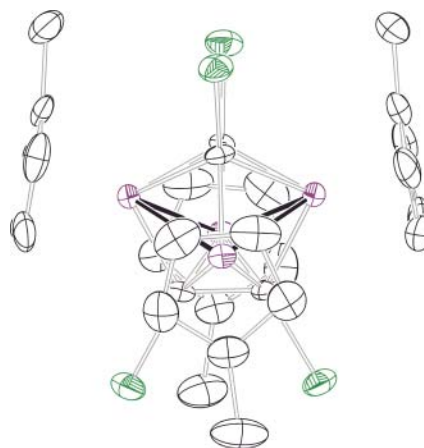
(C₆H₄OMe-*p*)₃, MePh₂, FPh₂) have been prepared by the reactions of *trans*-PtCl(SiR₃)(PMe₂Ph)₂ with Mg(CH=CH₂)₂ in THF, followed by *trans-cis* isomerization of the resulting *trans*-alkenyl(silyl) complexes in solution promoted by CO. The complexes undergo C-Si reductive elimination in toluene-*d*₈ to give platinum(0) complexes coordinated with vinylsilanes. Kinetic data have suggested a direct reaction path without dissociation of the phosphine ligand.



Scheme 2. C-Si Reductive elimination from Pt(II) complexes.

Synthesis and Property of BrCCH- and BrCCBr-Coordinated Tetrairon Clusters

Haloalkynes have been recognized as useful C₂ synthetic intermediates in organic chemistry. However, the coordination chemistry of haloalkynes has yet to be explored in detail. We succeeded in the stepwise bromination of two acetylene ligands in [(η^5 -C₅H₄Me)₄Fe₄(HCCH)₂]⁺ using *N*-bromosuccinimide (NBS). The bromoacetylene part displays high reactivities toward a variety of nucleophiles such as water, ZnR₂ (R=Me, Et), HC≡CMgBr, LiS^{*p*}Tol, pyridine, and 4,4'-bipyridyl.



Scheme 3. Molecular structure of [(η^5 -C₅H₄Me)₄Fe₄(BrCCHBr)₂]⁺.

Grants

Ozawa F, Reaction Control of Catalytic Intermediates, Grant-in-Aid for Scientific Research on Priority Areas, October 2002 - March 2006.

Ozawa F, Novel Organometallic Complexes with Phophaalkene Ligands: Synthesis and Catalysis, Grant-

in-Aid for Scientific Research (B) (2), April 2003 - March 2006.

Okazaki M, Chemistry of "Ethyne Cation"-Coordinated Transition-Metal Clusters, Grants-in-Aid for Young Scientists (B), April 2005 - March 2007.